

COATINGS. ENAMELS

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ELECTROCHEMICAL METHODS FOR IMPROVING THE STRENGTH OF ADHESION OF ONE-COAT GLASS ENAMELS TO SUBSTRATE

E. A. Yatsenko,¹ A. P. Zubekhin,¹ and E. B. Klimenko¹

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A method for pretreatment of steel surface before one-coat enameling is proposed, which makes it possible to obtain an enamel coating with sufficiently strong adhesion and good surface quality. The essence of this method is electrolytic precipitation of nickel and copper layers on steel surface. A composition of one-coat enamel coating based on aluminum-bearing waste has been developed. Tinted one-coat enamels have been obtained based on this composition.

Single-coat enameling without a primer currently occupies the leading position in the enameling industry. Using such enamels saves on materials and electricity and, accordingly, reduces the production cost of finished goods, which is essential in the contemporary market economy. A specific feature of one-coat enameling is the fact that in the absence of a primer, which is an adhesive layer, the single-layer enamel should combine the properties of undercoat and surface layers. Therefore, compounds facilitating good adhesion with metal are usually included in the composition of one-coat enamels. However, to achieve high quality and good adhesion to steel in a one-layer coating, it is not sufficient just to introduce adhesion oxides into the enamel composition. In one-coat enameling, the steel surface requires additional treatment, which is especially important for light-colored enamels.

The following methods of additional treatment of the metal surface before one-coat enameling are known: sandblasting, chemical nickel-plating, boronizing, and thermal treatment in combination with chemical nickel-plating; however, all these methods have disadvantages (environmental problems, warping of metal, unhealthy working conditions) and prevent obtaining high-quality single-layer coatings with sufficiently good adhesion.

For large-size enameled articles, the most promising method is depositing metal film on steel surface. There are several methods for depositing such films:

- immersion of articles into molten metal (hot method);
- cementing (thermal diffusion);
- metallizing with spray metal from a sprayer;

- contact method of metal precipitation;
- electrolytic method.

The electrolytic method for depositing metal film has become the most common in preparing steel surface for enameling, as this method has several advantages over other methods: a high degree of purity of electrolytically deposited metal; high chemical resistance of the metallic coating due to the purity of the precipitate; low metal consumption; possibility of precise control of coating thickness and duration of application; good mechanical properties of coating (elasticity and good adhesion to steel). Nickel plating is the traditional technique in one-coating enameling technology, however, we tested additionally zinc plating and copper plating.

Nickel plating is carried out with electrolytes, in which nickel mainly exists in the form of the bivalent cation Ni^{2+} . Apart from nickel salts, electrolytes also contain components intended for increasing conductivity, stabilizing acidity, improving solubility of anodes, and preventing various defects occurring in nickel plating (antipitting additives).

There exist various electrolytes for nickel plating [1]: sulfate, fluoboric, ammonium. Fluoboric electrolytes contain fluoboric nickel, nickel chloride, and boric acid and are characterized by high current strength; the coatings are light-colored, elastic, and sufficiently hard. However, the high cost of these chemical agents prevents wide application of these electrolytes. The ammonium electrolyte consists of nickel sulfate, ammonium sulfate, potassium chloride, ammonia, cadmium sulfate, and sodium fluoride. This electrolyte produces high strength of adhesion to metal, elasticity, and steady luster, but it is not widely used, since it contains toxic ammonia and ammonium sulfate. Sulfate electrolytes contain

¹ South-Russian State Technical University (NPI), Novocherkassk, Russia.

nickel sulfate, sodium sulfate, boric acid, and potassium chloride. In our case we used precisely the sulfate electrolyte, which has certain advantages, such as stable performance and high current strength.

Various electrolytes are used for zinc plating: acid, cyanide, zincate, and fluoboric. Electric precipitation of zinc as a rule is performed using cyanogen electrolytes. Acid electrolytes, due to some deficiencies, mainly their low scattering capacity, are mostly used in metallurgy for zinc-plating of products of simple configurations. However, in the context of more stringent requirements for ecological safety of technological processes, low-cyan, alkaline, and weakly acid electrolytes have been developed and are now commonly used.

The main components of the cyanide electrolyte are zinc cyanide or oxide, sodium (potassium) cyanide, and sodium (potassium) hydroxide. This electrolyte ensures a high-quality zinc precipitate under rather high current density, but is not widely used due to the toxicity of its components.

Acid electrolytes include zinc sulfate (less frequently zinc chloride, fluoboride, acetate) and buffer additives (aluminum and magnesium sulfates and chlorides), in whose presence the precipitate becomes lighter-colored and smoother. Using these electrolytes makes it possible to precipitate zinc at a high rate; the electrolytes are not expensive, and some of them have good scattering capacity. Fluoboric electrolytes are industrially used less frequently than sulfate and chloride ones due to their higher cost and a more complicated technology of preparation and application.

Zincate electrolytes have poorer technological parameters than cyanide and weakly acid electrolytes. Their defects include a high rate of dissolution of zinc anodes in the absence of current and under an excess of free alkali. These electrolytes are used when weakly acid or neutral zinc-plating electrolytes cannot be used for technical reasons (due to the absence of baths with acid-resistant lining) or in small galvanizing shops with a low output. In our research we used the ammoniate electrolyte, which has better scattering capacity than others, is less toxic than the cyanide electrolyte, and is suitable for zinc plating of small-sized parts and articles of a complicated relief.

Various electrolytes have been developed for electrical precipitation of copper [1]. They are all based on their composition, and the precipitating specifics are divided into two main groups: alkaline and acid. The group of alkaline electrolytes is headed by the cyanide electrolytes with the following composition: complex cyanide, sodium cyanide, caustic soda, and seignette salt. An acid copper-plating electrolyte consists of, for instance, copper sulfate, sulfuric acid, and ethyl alcohol.

Comparing the two main electrolytes cyanide and sulfate, the following differences should be noted. Precipitation of copper in cyanide electrolytes proceeds from complex copper-cyanide salts of potassium or sodium, and in a sulfate electrolyte from simple copper sulfate salt. In long service the use of cyanide electrolytes requires their frequent corre-

TABLE 1

Metal	ρ , g/cm ³	Y_c , %	E_k , g/(A · h)	δ , A/dm ²	Duration, sec, of applying film of thickness, μm		
					0.2	0.5	3.0
Nickel	8.90	96	1.095	1.5	40	100	601
Zinc	7.13	96	1.220	1.0	44	107	642
Copper	8.40	100	1.185	1.5	34	76	454

tion, especially regarding the content of free sodium cyanide. The sulfate electrolyte consisting only of copper sulfate and sulfuric acid is stable in service. At the same time, fluctuations in the concentration of components within a wide range are admissible. The cost of chemical agents for preparing a cyanide electrolyte is significantly higher. Furthermore, copper cyanide and sodium cyanide, which make up part of the cyanide electrolyte, are toxic. Consequently, cyanide electrolytes are regarded as an occupational hazard and their use requires special ventilation and strict compliance with service regulations. Sulfate electrolyte is not toxic and its application requires compliance with special safety rules only in the course of correction of sulfuric acid. In view of the above, we use acid copper-plating electrolyte for electrochemical treatment of metal in our research.

Before applying a metal layer to steel, the following stages are needed: degreasing, pickling, and washing. Degreasing was performed with Vienna lime, which is a product of firing of lime and dolomite containing at least 94.5% calcium oxide with small quantities of magnesium oxide, iron oxide, and other impurities. Pickling of steel was carried out in a hydrochloric acid solution (1 : 1) at room temperature for 3 min. After that steel was washed in running water and placed into the electrolyte solution. In accordance with a preset film thickness (0.2 – 3.0 μm), the duration of precipitation of coating was calculated from the formula

$$\tau = \frac{h\rho}{Y_c E_k I},$$

where τ is the duration of deposition of coating, h; h is the coating thickness, μm ; ρ is the coating density, g/cm³; Y_c is the current yield, %; E_k is the electrochemical equivalent, g/(A · h); I is the strength of current, A.

The strength of current was found from the formula

$$I = \delta S,$$

where δ is the current density, A/dm² and S is the surface area of the sample, dm².

The calculated values are listed in Table 1.

The effect of the type and thickness of metallic film on the strength of adhesion and the quality of enamel is shown in Table 2.

The glass formation area of synthesized enamels is located in the system $\text{R}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ –

TABLE 2

Electrolyte composition and operating conditions	Metallic film thickness, μm	Metal surface exterior		Surface quality of fired enamel coating			
		texture	color	color	luster, %	defects	adhesion strength, grade
20 – 40 g/liter $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	3.0	Dull	Silvery-white	Dark gray	10	Blisters	0
50 – 150 g/liter NH_4Cl	0.5	The same	Yellowish-gray	Gray	15	Pinholes	1
5 – 7 g/liter Novocor Ts	0.2	"	The same	Dirty white	15	The same	1
0.002 – 0.003 g/liter NPI 89							
pH = 7							
Temperature 16 – 30 °C							
250 – 300 g/liter $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	3.0	Lustrous	Silvery-white	The same	30	Blisters	1
6 – 10 g/liter $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	0.5	Dull	The same	White	35	Pinholes	2
25 – 35 g/liter H_3BO_3	0.2	The same	Gray	The same	40	The same	3
pH = 1							
Temperature 20 – 22 °C							
210 – 245 g/liter $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	3.0	Lustrous	Pink	Silvery-white	45	"	2
50 – 60 g/liter H_2SO_4	0.5	The same	Grayish-pink	White	44	–	4
3 – 6 g/liter $\text{C}_2\text{H}_5\text{OH}$	0.2	"	The same	The same	50	–	4
pH = 3.4							
Temperature 18 – 22 °C							
250 – 300 g/liter $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.1 : 0.1	"	"	"	50	Pinholes	3
6 – 10 g/liter $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$							
25 – 35 g/liter H_3BO_3							
pH = 1							
Temperature 20 – 22 °C							
210 – 245 g/liter $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.2 : 0.3	"	"	"	45	–	4
50 – 60 g/liter H_2SO_4							
3 – 6 g/liter $\text{C}_2\text{H}_5\text{OH}$							
pH = 3.4							
Temperature 18 – 22 °C							
	0.3 : 0.2	"	"	"	50	–	4

$\text{TiO}_2 - \text{MnO}_2 - \text{NiO} - \text{Fe}_2\text{O}_3 - \text{P}_2\text{O}_5$. The initial enamel has the following chemical composition (here and elsewhere wt.%): 30.67 SiO_2 , 14.60 B_2O_3 , 2.88 Al_2O_3 , 16.77 TiO_2 , 17.19 Na_2O , 7.08 K_2O , 8.36 Li_2O , 1.70 P_2O_5 , 0.10 NiO , 0.55 CaO , 0.075 Fe_2O_3 , 0.05 MnO_2 , and 0.15 F, which was obtained from batches of the low-melting undercoat and one-coat enamels synthesized earlier in a ratio of 5 : 95 (RF patent No. 2141458) [2].

Aluminum oxide is traditionally introduced into a glass batch via expensive raw materials: technical alumina, aluminum hydroxide, etc. A specific feature of our research consisted in replacing aluminum oxide by alumina-bearing waste generated at Belya Kalitva metallurgical works (Rostov Region). The chemical composition of the waste is as follows (%): 15.14 SiO_2 , 72.23 Al_2O_3 , 1.95 Fe_2O_3 , 1.77 CaO , 5.55 MgO , 0.32 TiO_2 , 0.052 MnO_2 , 2.22 K_2O , 1.59 Na_2O , and 3.46 Cl^- . The value of this waste is the high content of aluminum oxide (72.23%), due to which it can be used as an alumina-bearing material. According to the results of our study, the majority of the components in this waste exist in the more active amorphous state, and, consequently, in a glass batch they act as fluxes, which lowers the melting temperature of enamel frit and the firing temperature of the glass-enamel coating. The presence of manganese oxide in

this waste makes it possible to decrease viscosity and surface tension and increase spreadability of enamel in firing and thus to increase the strength of adhesion of enamel coating to metal and improve the quality of enamel coating, since manganese oxide in a glass melt acts as a surfactant. All this contributes to lowering the cost of materials and power and, subsequently decreasing the production cost of finished product, which is essential in a market economy.

The batch was prepared from traditional raw materials used in the glass industry (sand, soda, etc.), the only exception being the alumina-bearing waste. The frits were melted in alundum crucibles in an electric furnace with silit heaters at a maximum temperature of 1250°C with an exposure of 30 – 40 min. Melted glass was cooled in water, then a slip was prepared using the traditional method.

Steel with the metal coating on it was dried and covered by enamel slip using the casting method. After that the samples were dried in a drying cabinet at 100°C and then the one-coat enamel was fired at 770°C. The external aspect of enamel coating was evaluated (luster, presence of defects) and the strength of adhesion of enamel to metal was measured and graded (GOST 24788–81). The obtained results are shown in Fig. 1.

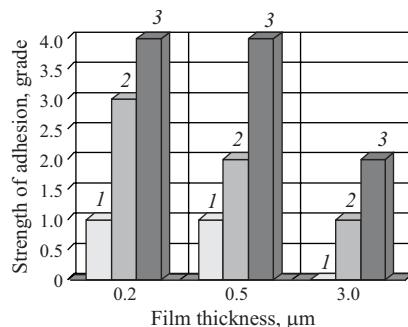


Fig. 1. Dependence of strength of adhesion of enamel on film thickness of zinc (1), nickel (2), and copper (3).

TABLE 3

Oxide introduced above 100%	Mass content, %	Color of enamel
Initial composition	—	White
CoO	1.0	Deep blue
NiO	0.5	Snowy white
Fe ₂ O ₃	1.0	Light gray
MnO ₂	1.5	Beige
Cu ₂ O	1.5	Blue quartz
Cr ₂ O ₃	1.0	Lettuce-green

It can be seen that the optimum thickness of all types of metallic films is 0.2 μm, since increasing thickness to 0.5 μm does not change the results and on further growth of thickness the adhesion of enamel to the film and, accordingly, to steel deteriorates perceptibly. Furthermore, the best adhesion strength is registered in enamel coatings deposited on the copper-plated steel surface. However, precipitation of copper film on steel is technologically unstable. In the drying of enamel coating, the copper film may exfoliates from the steel surface. To remove this defect, we developed a method for complex deposition of copper film upon a nickel film with the following thickness ratios: 0.1 : 0.1, 0.3 : 0.2, and 0.2 : 0.3 μm. The complex deposition of films not only increases the strength of adhesion of enamel to metal (grade 4), but also improves the adhesion of copper film to steel due to the deposition of the nickel film. The optimum ratio of metal films layers is 0.3 : 0.2 μm (Table 2).

The increased strength of adhesion in this case is due to the fact that the transitional copper-enamel layer contains such phases as CuO · SiO₂ and CuO, which, presumably, like fayalite (iron silicate), have the spinel structure and participate in adhesion of enamel to copper and, accordingly, to steel. This is corroborated by the results of the optical-microscope studies of the transitional layers on the steel – metallic film – enamel boundaries (Fig. 2).

To obtain low-melting tinted enamels, oxides of *d*-elements (CoO, NiO, Fe₂O₃, MnO₂, Cu₂O) were introduced

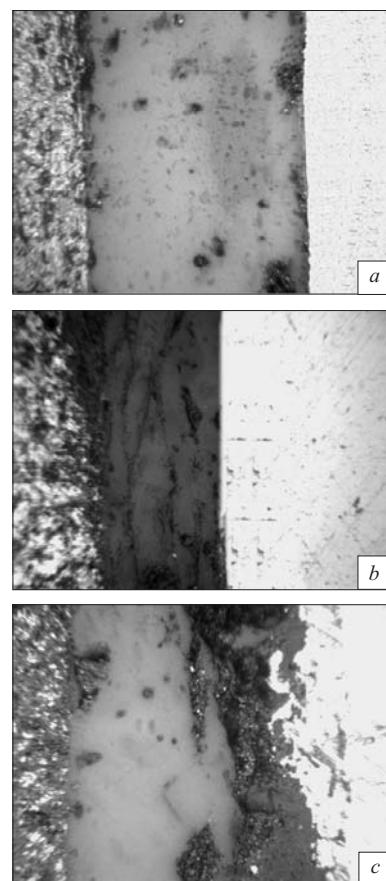


Fig. 2. Microphotos of transitional layers in one-coat enamels at steel – metal film – enamel interface ($\times 1000$): a) nickel film 0.5 μm thick; b) zinc film 0.2 μm thick; c) complex nickel – copper film with thickness ratio 0.3 : 0.2 μm.

(above 100%). The colors of one-coat enamels for steel are indicated in Table 3.

Thus, just correcting the chemical composition of coating is insufficient for obtaining a high-quality single-layer coating. The method for preparing metal surface is very important. The optimum among all electrochemical methods is the deposition of a complex thin-gage (0.3 – 0.2 μm) nickel – copper film on steel surface, which substantially increases the strength of adhesion and improves the quality of the enamel coating.

The colors obtained make it possible to expand areas of application of one-coat glass-enamel coatings and improve their aesthetic and consumer properties.

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